



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Stoichiometric changes to $\text{KH}_2\text{PO}_4$ during laser-induced breakdown

R. A. Negres, S. O. Kucheyev, P. DeMange, C.  
W. Carr, S. G. Demos

November 19, 2004

Boulder Damage Symposium 2004  
Boulder, CO, United States  
September 20, 2004 through September 22, 2004

## **Disclaimer**

---

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

# Stoichiometric changes to $\text{KH}_2\text{PO}_4$ during laser-induced breakdown

R. A. Negres, S. O. Kucheyev, P. DeMange, C. W. Carr and S. G. Demos

Lawrence Livermore National Laboratory  
PO Box 808, L-370, Livermore, CA 94551, USA

## ABSTRACT

The local structure of  $\text{KH}_2\text{PO}_4$  crystals (so-called KDP) at laser-induced damage sites created by irradiation with  $\sim 3$ -ns, 355-nm laser pulses is studied by a combination of Raman scattering and photoluminescence spectroscopies. We compare spectra from pristine material, surface and bulk laser-induced damage sites, as well as from  $\text{KPO}_3$  references. Results show that irradiation with fluences above the laser-induced breakdown threshold leads to stoichiometric changes at surface damage sites but not at bulk damage sites. New spectroscopic features are attributed to dehydration products. For the laser irradiation conditions used in this study, the decomposed near-surface layer absorbs photons at  $\sim 3.4$  eV (364 nm). These results may help explain the recently reported observation that surface laser damage sites in KDP crystals tend to grow with subsequent exposure to high-power laser pulses, while bulk damage sites do not.

**Keywords:** Laser-induced damage, KDP and DKDP crystals, Raman spectroscopy, photoluminescence, condensed phosphates

## 1. INTRODUCTION

Potassium dihydrogen phosphate, KDP ( $\text{KH}_2\text{PO}_4$ ), is a transparent dielectric material widely used for frequency conversion and optoelectronic switching in laser systems.<sup>1</sup> In addition, KDP can be conveniently grown as a single crystal with large linear dimensions (50 – 100 cm), as required for large-aperture high-power lasers.<sup>1–3</sup> However, the output of such laser sources can be limited by the optical performance of various components under high-power laser irradiation, which suffer from laser-induced damage (LID) both at the surface and in the bulk.<sup>3</sup>

It is currently believed by many researchers that absorption by intrinsic and/or extrinsic defects present in the bulk or at the surface of the material is responsible for damage initiation.<sup>4–6</sup> Material defects may be found in every optical component resulting from limitations in the manufacturing process or the environmental or excitation conditions during its operation.<sup>6–9</sup> A damage site on the surface of an optical material generated with nanosecond laser sources usually appears as a crater with rough surfaces that strongly scatter the incoming laser beam. It has been shown that the laser damage process leads to the formation of a layer of modified material inside the damage crater.<sup>10–12</sup> The damage site can nominally include three different sectors: a layer with a modified chemical composition, a layer of mechanically damaged material (crushed, compressed) and a surrounding region of extended cracks. Although numerous previous studies have focused on the mechanisms of LID initiation in as-grown KDP crystals, the properties of the material modified during laser-induced breakdown have received little attention. It is, however, crucial to understand the properties of laser-modified KDP since it may be involved in the damage “reignition” and process growth of LID sites with subsequent exposure to laser pulses.

In this work, we investigate laser-induced structural and stoichiometric changes in KDP crystals by a combination of Raman scattering and photoluminescence (PL) spectroscopies. These spectroscopic tools are sensitive to the local structure and bonding in the solid.<sup>13</sup> Our results reveal that irradiation leads to changes in material stoichiometry at surface LID sites but not at bulk damage sites. We attribute the new Raman features observed to dehydration products being present at surface damage sites due to laser-induced decomposition of a near-surface layer of KDP into water and a mixture of solid poly- and cyclo-phosphates. This can explain recent observations that surface LID sites in KDP tend to grow with subsequent laser pulses,<sup>14</sup> whereas bulk LID sites do not,<sup>15</sup> and provide the knowledge to devise the appropriate mitigation procedures.

---

Send correspondence to R. A. Negres: E-mail: negres2@llnl.gov, Telephone: 1 925 423 1425, Fax: 1 925 423 0909

## 2. EXPERIMENT

The *z*-cut [i.e., (001)-oriented] tetragonal  $\text{KH}_2\text{PO}_4$  single crystals used in this study were grown by a rapid growth method at Lawrence Livermore National Laboratory, as described in detail elsewhere.<sup>3</sup> As-received KDP samples were polished with  $\text{H}_2\text{O}$ . The reference  $\text{KPO}_3$  salt was prepared by annealing KDP crystals at 350 °C for 3 hours in air. The dehydrated salt prepared in this way was composed of a mixture of cyclophosphates and long-chain polyphosphates.<sup>16</sup>

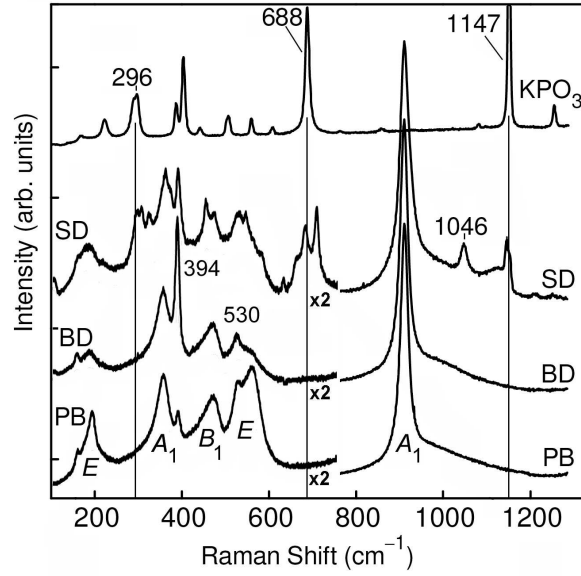
Laser-induced damage sites were created on the front surface and in the bulk of KDP crystals by irradiation (at room temperature and ambient conditions) with  $\sim 3$ -ns, 355-nm pulses from a *Q*-switched Nd:YAG laser. The laser beam profile at the sample plane was near-Gaussian with a FWHM of  $\sim 20 \mu\text{m}$  and a peak fluence of  $\sim 20 \text{ J/cm}^2$ . In order to minimize nonuniformities in the damaged volume, both surface and bulk damage regions,  $\geq 1 \times 1 \text{ mm}^2$  in size, were created by slowly scanning the sample through the focused damaging beam so that each LID site has been exposed to multiple ( $\sim 20$ ) pulses.

These LID sites were studied at room temperature by a combination of Raman and PL spectroscopies. Emission lines of a *cw* Ar laser, at 363.8 and 514.5 nm, were used as excitation sources for PL and Raman measurements, respectively. Both Ar laser lines were passed through narrow band pass filters before reaching the sample in order to eliminate the appearance of plasma lines. The Raman experiment was performed in a back-scattering geometry using a  $\times 100$  microscope objective for both focusing the laser beam and collecting the Raman signal, which was then spectrally analyzed using a triple-grating spectrograph and recorded with a liquid-nitrogen-cooled CCD. The numerical aperture of the objective was 0.7 and provided  $\sim 1 \mu\text{m}$  and  $\sim 5 \mu\text{m}$  lateral and depth resolution, respectively. Raman spectra of KDP were normalized to the peak intensity of the  $\text{H}_2\text{PO}_4$  mode at  $911 \text{ cm}^{-1}$ . The PL signal was collected into a single-grating spectrograph using a 2:1 imaging system positioned perpendicularly to the direction of the 363.8 nm laser beam. All PL spectra were corrected for the system response.

## 3. RESULTS AND DISCUSSION

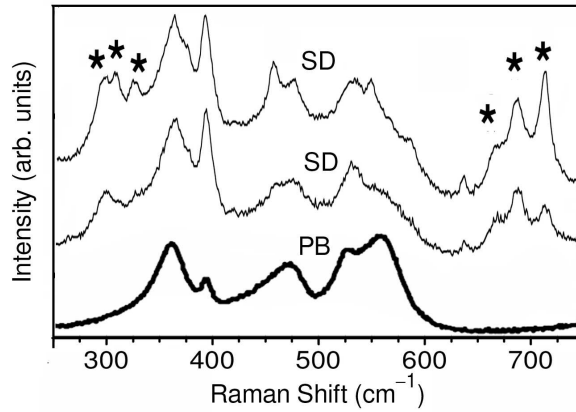
Figure 1 compares Raman spectra obtained from pristine bulk (labelled PB) KDP, bulk and surface LID sites (labelled BD and SD, respectively) in KDP, as well as from a  $\text{KPO}_3$  reference. The Raman-active modes of KDP belong to the  $A_1$  (360 and  $911 \text{ cm}^{-1}$ ),  $B_1$  ( $476 \text{ cm}^{-1}$ ),  $B_2$  (not observed) and  $E$  ( $190$  and  $565 \text{ cm}^{-1}$ ) representations of the factor group  $D_{2d}$ .<sup>17</sup> The most prominent bands between  $300$  and  $1200 \text{ cm}^{-1}$  in the PB spectrum (which is essentially identical to Raman spectra from the surface of pristine KDP) are due to internal vibrations of  $\text{H}_2\text{PO}_4$  units while the bands below  $200 \text{ cm}^{-1}$  are lattice modes. In addition, we observe two modes at  $394 \text{ cm}^{-1}$  ( $B_1$ ) and  $530 \text{ cm}^{-1}$  ( $E$ ), overshadowed by the adjacent stronger bands. It is seen from Fig. 1 that the Raman spectrum from a bulk damage site does not exhibit any new peaks as compared to the spectrum from pristine KDP. The relative peak intensities of the bands at  $394 \text{ cm}^{-1}$  and  $530 \text{ cm}^{-1}$  are, however, significantly different in PB and BD spectra, indicating some structural changes and/or the presence of residual lattice stress produced during laser-induced breakdown.

Figure 1 also shows that Raman spectra from surface LID sites exhibit four new bands centered on 296, 688, 1046, and  $1147 \text{ cm}^{-1}$ . In addition, changes in the relative intensities of the KDP-related peaks are observed similar to those in bulk damage sites. These new Raman features are evidence of laser-induced changes in material *stoichiometry*. The origin of the new peaks can be understood when we compare the SD spectrum with that from a  $\text{KPO}_3$  reference. The latter spectrum consist of a series of well-defined, narrow vibrational modes, suggesting a crystalline phase. Indeed, three out of four new bands observed in SD spectra (at 296, 688, and  $1147 \text{ cm}^{-1}$ ) correlate to peaks present in the  $\text{KPO}_3$  spectrum. The band centered at  $1147 \text{ cm}^{-1}$  exhibits a single dominant peak. Furthermore, the same Raman features have been observed prior to our work in the context of high-temperature behavior of KDP.<sup>18</sup> The interpretations have been diverse over the years but recent studies have confirmed that high-temperature phenomena in KDP are not related to the structural phase transition but rather to the thermal decomposition (condensation and polymerization of  $\text{PO}_4$  groups).<sup>18, 19</sup> The other peak at  $1046 \text{ cm}^{-1}$ , observed in SD but not in the  $\text{KPO}_3$  spectrum, has previously been reported in Raman studies of the  $\text{K}_2\text{O-P}_2\text{O}_5$  glass system and assigned to polyphosphates with longer  $\text{PO}_4$  chains.<sup>20</sup> The formation of these latter products requires processing temperatures in excess of 350 °C, the annealing temperature used in this study to prepare  $\text{KPO}_3$  reference samples.



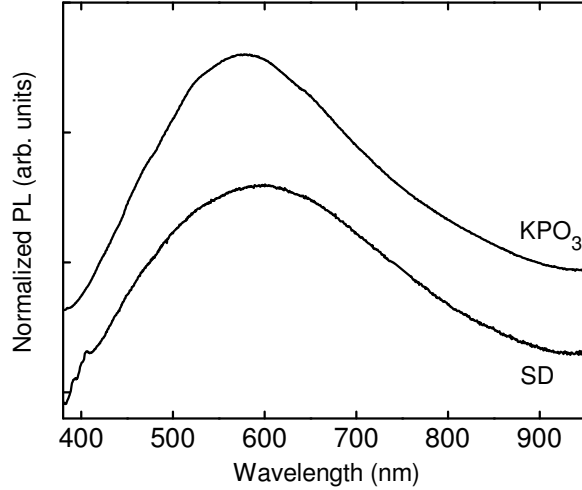
**Figure 1.** Typical Stokes Raman spectra from KDP at various locations: pristine bulk (PB) (i.e., undamaged), bulk and surface damage sites (BD and SD, respectively). A spectrum from  $\text{KPO}_3$  is also shown for comparison. All spectra are unpolarized and offset for clarity.

The Raman signal slightly varied at different sites within the surface damage region. This effect is demonstrated in the two representative spectra shown in more detail in Fig.2. It is seen from this graph that the bands around  $296$  and  $688\text{ cm}^{-1}$  exhibit additional splitting into individual peaks located at  $296, 308, 326\text{ cm}^{-1}$  and  $636, 668, 688, 714\text{ cm}^{-1}$ , respectively (as indicated by asterisks). These results clearly demonstrate that changes to KDP during laser-induced breakdown are more complex than relatively simple material decomposition into water and  $\text{KPO}_3$  salt.



**Figure 2.** KDP Raman spectra from two representative surface damage sites (SD), expanded in the  $250 - 750\text{ cm}^{-1}$  region. A spectrum from pristine bulk (PB) is also shown for comparison.

Figure 3 shows normalized PL spectra under  $363.8\text{ nm}$  excitation revealing a broad PL band centered on  $\sim 570 - 590\text{ nm}$  in both  $\text{KPO}_3$  and surface LID sites in KDP. Such broad emission originates from radiative recombination through deep defect levels in KDP and  $\text{KPO}_3$  rather than from band-to-band radiative recombination. It should be noted that i) a series of relatively sharp peaks observed in PL spectra from surface damage sites at wavelengths below  $415\text{ nm}$  are Raman scattering peaks and ii) PL signal from bulk LID sites (as well



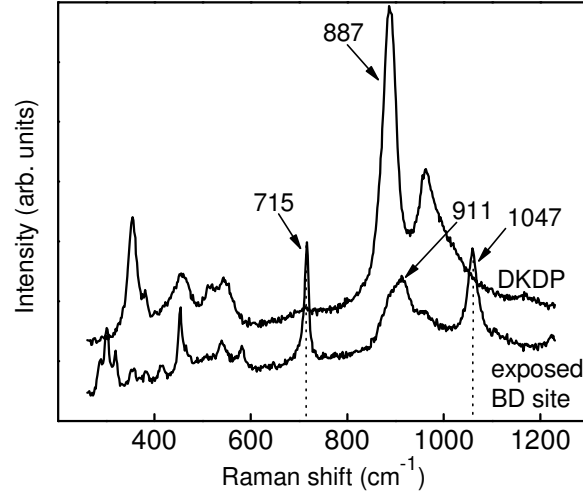
**Figure 3.** Normalized PL spectra [light intensity (in arbitrary units) versus wavelength (in nm)] from surface damage sites (SD) and KPO<sub>3</sub>. Spectra are offset for clarity.

as from pristine KDP) was much weaker, at least  $\times 100$ . Hence, these PL results not only support the presence of decomposition products at surface LID sites (as revealed by Raman spectroscopy) but also provide evidence that such decomposition products absorb UV light (i.e., the 363.8 nm light used for PL excitation).

The presence of dehydration products — condensed phosphates with a reduced relative composition of oxygen and hydrogen — at surface LID sites, as revealed in this study, can be attributed to thermally-induced decomposition of KDP during laser-induced breakdown. It should be noted that our results from Raman and PL spectroscopies are in good agreement with X-ray absorption studies in KDP crystals, where KPO<sub>3</sub> peaks were also identified in the total-electron-yield and total-fluorescence-yield XANES (soft x-ray absorption near-edge structure) spectra from surface damage sites (to be published). Indeed, it is known that thermal processing of KDP at temperatures above  $\sim 175$  °C results in material decomposition into water and KPO<sub>3</sub> salt, and the decomposition rate increases with increasing sample temperature.<sup>16,19</sup> A recent experimental study<sup>21</sup> has suggested temperatures of  $\sim 7000$  K at 10 ns after the laser pulse and pressures of  $\sim 250$  kbar in a deuterated KDP crystal exposed to an  $\sim 3$ -ns, 355-nm laser pulse. At such temperatures (well above the melting point of KDP at  $\sim 260$  °C),<sup>22</sup> thermally-induced decomposition is not unexpected, particularly at the sample surface. Although the intermediate steps involved in such an ultrafast reaction cannot be inferred from a post-damage event analysis, it is safe to assume that the fast cooling after damage can lead to residual stress in the modified material. This effect may be responsible for the observed splitting of the KPO<sub>3</sub> lines in the Raman spectra from surface LID sites. Moreover, as discussed above, the changes in the relative intensities of the KDP Raman features from both surface and bulk damage sites can also be the result of rapid recrystallization and residual lattice stress.

In contrast, decomposition at bulk LID sites appears to be hindered due to the encapsulation by the surrounding material. The fact that we have not observed any signature of stoichiometric changes in the Raman spectra from bulk LID sites in KDP can also be related to an increased scattering of excitation light at micro-cracks surrounding the laser damage core. In order to clarify this point, experiments that offer higher spatial resolution are required.

Preliminary results<sup>23</sup> have been obtained in micro-Raman measurements from "exposed" bulk damage sites in DKDP crystals. In order to gain access to bulk LID sites, samples were prepared by "cleaving" a DKDP sample containing bulk damage, previously created by exposure to  $\sim 3$ -ns, 355-nm laser pulses. Figure 4 illustrates Raman spectra from two particular sites, pristine bulk and exposed BD sites in DKDP. More details on sample preparation can be found in Ref. 23. The Raman spectrum of DKDP shows the typical double-peak signature, at 887 and 963  $\text{cm}^{-1}$ , derived from the KDP Raman mode at 911  $\text{cm}^{-1}$  upon deuteration. New peaks are present in spectra from exposed bulk damage sites and the most prominent are indicated in Fig. 4, at 715 and 1047



**Figure 4.** Raman spectra from DKDP at two different locations: pristine bulk and exposed BD sites.

$\text{cm}^{-1}$ , similar to those observed in Raman spectra from SD sites in KDP. However, the KDP mode at  $911\text{ cm}^{-1}$  is also present in spectra from DKDP bulk damage sites, indicating D-H exchange at the surface of the exposed sites. It can be argued that the modified material at bulk damage sites was created by secondary reactions upon cleaving of the sample and/or after the exposure in the air and not during the LID process. At this point, the interpretation of the spectra is somewhat cumbersome, partly because of the mixed KDP/DKDP Raman features, and more experiments are needed to correctly address this issue.

#### 4. SUMMARY

We have shown that irradiation of KDP with  $\sim 3\text{-ns}$ ,  $355\text{-nm}$  laser pulses with fluences above the laser-induced breakdown threshold leads to stoichiometric changes (attributed to laser-induced material decomposition) at surface damage sites but not at bulk damage sites. The decomposed near-surface layer absorbs  $364\text{-nm}$  UV light. Hence, this work provides more insight into the physics of the LID process in KDP crystals in that it differentiates between the behavior of surface and bulk damage sites. These results may help explain the recently reported observation that only surface laser damage sites in KDP crystals tend to grow with subsequent exposure to high-power laser pulses. We conclude that a proper procedure for mitigation of surface damage growth in KDP crystals should involve the removal of the laser-modified material by, for example, etching.

#### ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

#### REFERENCES

1. L. N. Rashkovich, *KDP-Family Single Crystals*, Adam Hilger, Bristol, 1991.
2. N. Zaitseva and L. Carman, "Rapid growth of KDP-type crystals," *Prog. Cryst. Growth Charact. Mater.* **43**, pp. 1–118, 2001.
3. J. J. De Yoreo, A. K. Burnham, and P. K. Whitman, "Developing  $\text{KH}_2\text{PO}_4$  and  $\text{KD}_2\text{PO}_4$  crystals for the world's most powerful laser," *Int. Mater. Rev.* **47**, pp. 113–152, 2002.
4. D. Ehrt, P. Ebeling, and U. Natura, "UV Transmission and radiation-induced defects in phosphate and fluoride-phosphate glasses," *J. Non-Cryst. Solids* **263&264**, pp. 240–250, 2000.
5. S. G. Demos and M. Staggs, "Application of fluorescence microscopy for noninvasive detection of surface contamination and precursors to laser-induced damage," *Appl. Opt.* **41**, pp. 1977–1983, 2002.

6. S. G. Demos, M. Staggs, and H. B. Radousky, "Bulk defect formations in  $\text{KH}_2\text{PO}_4$  crystals investigated using fluorescence microscopy," *Phys. Rev. B* **67**, p. 224102, 2003.
7. J. E. Davis, R. S. Hughes Jr., and H. W. H. Lee, "Investigation of optically generated transient electronic defects and protonic transport in hydrogen-bonded molecular-solids - isomorphs of potassium dihydrogen phosphate," *Chem. Phys. Lett.* **207**, pp. 540–545, 1993.
8. C. D. Marshall, S. A. Payne, M. A. Henesian, J. A. Speth, and H. T. Powell, "Ultraviolet-induced transient absorption in potassium dihydrogen phosphate and its influence on frequency-conversion," *JOSA B* **11**, pp. 774–785, 1994.
9. M. M. Chirila, N. Y. Garces, L. E. Halliburton, S. G. Demos, T. A. Land, and H. B. Radousky, "Production and thermal decay of radiation-induced point defects in  $\text{KD}_2\text{PO}_4$  crystals," *J. Appl. Phys.* **94**, pp. 6456–6462, 2003.
10. M. R. Kozlowski, C. L. Battersby, and S. G. Demos, "Luminescence investigation of  $\text{SiO}_2$  surfaces damaged by  $0.35\text{ }\mu\text{m}$  laser illumination," in *Laser-Induced Damage in Optical Materials: 1999*, G. J. Exarhos, A. H. Guenther, M. R. Kozlowski, K. L. Lewis, and M. J. Soileau, eds., *Proc. SPIE* **3902**, pp. 138–143, 2000.
11. S. G. Demos, M. Staggs, and H. B. Radousky, "Laser induced material modification in the bulk KDP crystals," in *Laser-Induced Damage in Optical Materials: 1999*, G. J. Exarhos, A. H. Guenther, M. R. Kozlowski, K. L. Lewis, and M. J. Soileau, eds., *Proc. SPIE* **3902**, pp. 428–432, 2000.
12. S. O. Kucheyev and S. G. Demos, "Optical defects produced in fused silica during laser-induced breakdown," *Appl. Phys. Lett.* **982**, pp. 3230–3232, 2003.
13. G. J. Exarhos, *Characterization of Optical Materials*, Butterworth-Heinemann, Boston, 1993.
14. S. G. Demos, M. Staggs, and M. R. Kozlowski, "Investigation of processes leading to damage growth in optical materials for large-aperture lasers," *Appl. Opt.* **41**, pp. 3628–3633, 2002.
15. C. W. Carr, T. H. McMillian, M. Staggs, H. B. Radousky, and S. G. Demos, "Evolution of bulk damage initiation in DKDP crystals," in *Laser-Induced Damage in Optical Materials: 2002*, G. Exarhos, A. Guenther, N. Kaiser, K. Lewis, M. Soileau, C. Stolz, A. Giesen, and H. Weber, eds., *Proc. SPIE* **4932**, pp. 429–433, 2003.
16. A. Durif, *Crystal Chemistry of Condensed Phosphates*, Plenum, New York, 1995.
17. D. K. Agrawal and C. H. Perry, "The temperature dependent Raman spectra of KDP,  $\text{KD}^*\text{P}$ , KDA and ADP," in *Light Scattering in Solids*, M. Balkanski, ed., pp. 429–435, 1971.
18. J. A. Subramony, B. J. Marquardt, J. W. Macklin, and B. Kahr, "Reevaluation of Raman spectra for  $\text{KH}_2\text{PO}_4$  high-temperature phases," *Chem. Mater.* **11**, pp. 1312–1316, 1999.
19. K.-S. Lee, "Hidden nature of the high-temperature phase transitions in crystals of  $\text{KH}_2\text{PO}_4$ -type: is it a physical change?," *J. Phys. Chem. Solids* **57**, pp. 333–342, 1996.
20. A. V. Baranov, V. V. Golubkov, and V. I. Petrov, "Structural investigations of pyrophosphate glasses by Raman spectroscopy and small-angle X-ray scattering," *Glass Phys. Chem.* **25**, pp. 291–303, 1999.
21. C. W. Carr, H. B. Radousky, M. Staggs, A. M. Rubenchik, M. D. Feit, and S. G. Demos, "Time-resolved spectroscopic investigation of emission observed during damage in the bulk of fused silica and DKDP crystals," in *Laser-Induced Damage in Optical Materials: 2001*, G. Exarhos, A. Guenther, K. L. Lewis, M. J. Soileau, and C. J. Stolz, eds., *Proc. SPIE* **4679**, pp. 360–367, 2002.
22. E. Rapoport, J. B. Clark, and P. W. Richter, "High-pressure phase relations of  $\text{RbH}_2\text{PO}_4$ ,  $\text{CsH}_2\text{PO}_4$ , and  $\text{KD}_2\text{PO}_4$ ," *J. Solid State Chem* **24**, pp. 423–433, 1978.
23. C. W. Carr, M. D. Feit, J. J. Muyco, and A. M. Rubenchik, "Effect on scattering of complex morphology of DKDP bulk damage sites," this SPIE proceedings.